

US EPA ARCHIVE DOCUMENT

Supplemental Information

The following supplemental information is provided for -

Corrosion in a STP Sump: What Causes It and What Can Be Done About It?

Part 1. The identification numbers of the sumps, the corrosion scores of each sump, and the concentrations of ethanol and acetate in the passive diffusion samplers. -----Page 2

Part 2. Photographs of the sumps that were scored. -----Page 6

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Part 1. Raw data by sump, including the scores for presence or absence of corrosion, whether the sump was wet or dry, the concentration of ethanol and acetate in water in the sump (if present) and the concentration of ethanol and acetate that would be expected in condensation water on fixtures in the sump.

Sump #	Blue Corrosion	Rust Tubercles	Free Water In Sump at sometime during sampling	Sump dry	Ethanol In Vapor Sampler divided by 0.37	Acetate In Vapor Sampler divided by 0.067	Ethanol In Sump Water	Acetate In Sump Water
					(mg/L)	(mg/L)	(mg/L)	(mg/L)
2	No Evidence	No	Yes		0.78	0.15	0.023	4.93
3	No Evidence	No	Yes		6.76	0.15	0.023	4.6
4	Thick Blue Corrosion	Yes	Yes		72432.43	11671.64		
5	Thick Blue Corrosion	Yes	Yes		38108.11	9910.45		
7	Uniform Blue Coating	Yes	Yes		25.16	44.03	1.9	1.4
8	Uniform Blue Coating	Yes	Yes		39189.19	1835.82		
9	No Evidence	No		Yes	4.62	4.93		
10	No Evidence	No		Yes	71.89	0.15		
11	No Evidence	No	Yes		22.95	14.73	0.023	0.354
12	No Evidence	No		Yes	1.31	0.15		
13	No Evidence	No		Yes	0.06	0.15		
14	No Evidence	No		Yes	2.11	1.99		
15	cannot score	No		Yes	3459.46	3.85		

Sump #	Blue Corrosion	Rust Tubercles	Free Water In Sump at sometime during sampling	Sump dry	Ethanol In Vapor Sampler divided by 0.37	Acetate In Vapor Sampler divided by 0.067	Ethanol In Sump Water	Acetate In Sump Water
					(mg/L)	(mg/L)	(mg/L)	(mg/L)
16	cannot score	cannot score	Yes		55945.95	352.24	95900	3870
17	Uniform Blue Coating	No	Yes		153.78	3358.21	123	1630
18	cannot score	cannot score	Yes		25567.57	3656.72		
19	cannot score	No	Yes		9.38	0.15	0.154	9.43
20	No Evidence	No	Yes		6270.27	441.79	2990	461
21	No Evidence	No		Yes	689.19	69.55		
22	Thick Blue Corrosion	Yes	Yes		38918.92	23880.60	8280	72000
23	No Evidence	No		Yes	0.06	5.03		
24	Thick Blue Corrosion	Yes	Yes		59729.73	1791.04	17400	1850
25	No Evidence	No	Yes		2.11	67.91	14.8	No sample
26	Uniform Blue Coating	Yes		Yes	7378.38	1316.42		
27	cannot score	cannot score	Yes		0.06	0.15	0.735	0.01

Sump #	Blue Corrosion	Rust Tubercles	Free Water In Sump at sometime during sampling	Sump dry	Ethanol In Vapor Sampler divided by 0.37 (mg/L)	Acetate In Vapor Sampler divided by 0.067 (mg/L)	Ethanol In Sump Water (mg/L)	Acetate In Sump Water (mg/L)
29	steel	cannot score	Yes		2397.30	72.69	919	114
30	cannot score	cannot score	Yes		no sample	no sample		
31	cannot score	cannot score	Yes		no sample	no sample		
32	No Evidence	cannot score	Yes		no sample	no sample		
33	No Evidence	cannot score	Yes		120.54	67.31		
34	cannot score	cannot score	Yes		13.62	2.37		
35	cannot score	cannot score	Yes		13.86	70.90		
36	No Evidence	No		Yes	813.51	137.76		
37	Thick Blue Corrosion	Yes	Yes		79459.46	45074.63		
38	No Evidence	No	Yes		61351.35	13268.66		
39	Thick Blue Corrosion	Yes	Yes		15648.65	7417.91	529	6910

Sump #	Blue Corrosion	Rust Tubercles	Free Water In Sump at sometime during sampling	Sump dry	Ethanol In Vapor Sampler divided by 0.37	Acetate In Vapor Sampler divided by 0.067	Ethanol In Sump Water	Acetate In Sump Water
					(mg/L)	(mg/L)	(mg/L)	(mg/L)
40	No Evidence	No	Yes		16702.70	255.22	5.55	8.9
41	Thick Blue Corrosion	Yes	Yes		6.32	0.15		
42	No Evidence	No		Yes	4.03	74.78		
43	No Evidence	No		Yes	79729.73	4388.06		
44	No Evidence	No		Yes	0.19	0.15		
45	No Evidence	No		Yes	0.06	0.15		
46	Uniform Blue Coating	Yes		Yes	1108.11	1626.87		
47	cannot score	Yes		Yes	14189.19	6358.21		
48	Thick Blue Corrosion	Yes	Yes		56756.76	67611.94		
49	No Evidence	No	Yes		2.32	2.27	6.85	91.7
50	Thick Blue Corrosion	Yes	Yes		7783.78	6119.40	6010	10800

Part 2. Sumps that were scored.

Sump 2

Premium Gasoline

10/29/2010



Sump 3

Regular Gasoline

10/29/2010



Sump 4

Premium Gasoline

11/01/2010



Sump 5

Regular Gasoline

11/01/2010



Sump 7

Regular Gasoline

10/29/2010



Sump 8

Premium Gasoline

10/29/2010



Sump 9

Regular Gasoline

10/29/2010



Sump 10

Premium Gasoline

10/29/2010



Sump 11

Regular Gasoline

8/25/2010

The stp sump has metal flex piping with isolation coating (roskote) and solid anode installed to protect piping from corrosion. The stp pump piping is 5 plus years old.



Sump 12

Premium Gasoline

12/08/2010



Sump 13

Regular Gasoline

9/24/2010



Sump 14

E85 Gasoline

12/08/2010



Sump 15

E85 Gasoline

12/08/2010

Note from state regulator that collected the samples. The last round of samplers contained surprising results, the results show high ethanol vapors. This is surprising to me since the sump is a suction sump, and not seeing major corrosion. The site is a state facility recently converted to e-85. There might have been an ethanol odor when I gathered samplers in December (I will go back by the business with our explosively meter).



Sump 17

Premium Gasoline

3/7/2011



Sump 19

Regular Gasoline

2/4/2011



Sump 20

Regular Gasoline

3/7/2011



Sump 21

Premium Gasoline

3/7/2011



Sump 22

Premium Gasoline

4/18/2011



Sump 23

Regular Gasoline

6/16/2011



Sump 24

Premium Gasoline

3/29/2011



Sump 25

Diesel fuel

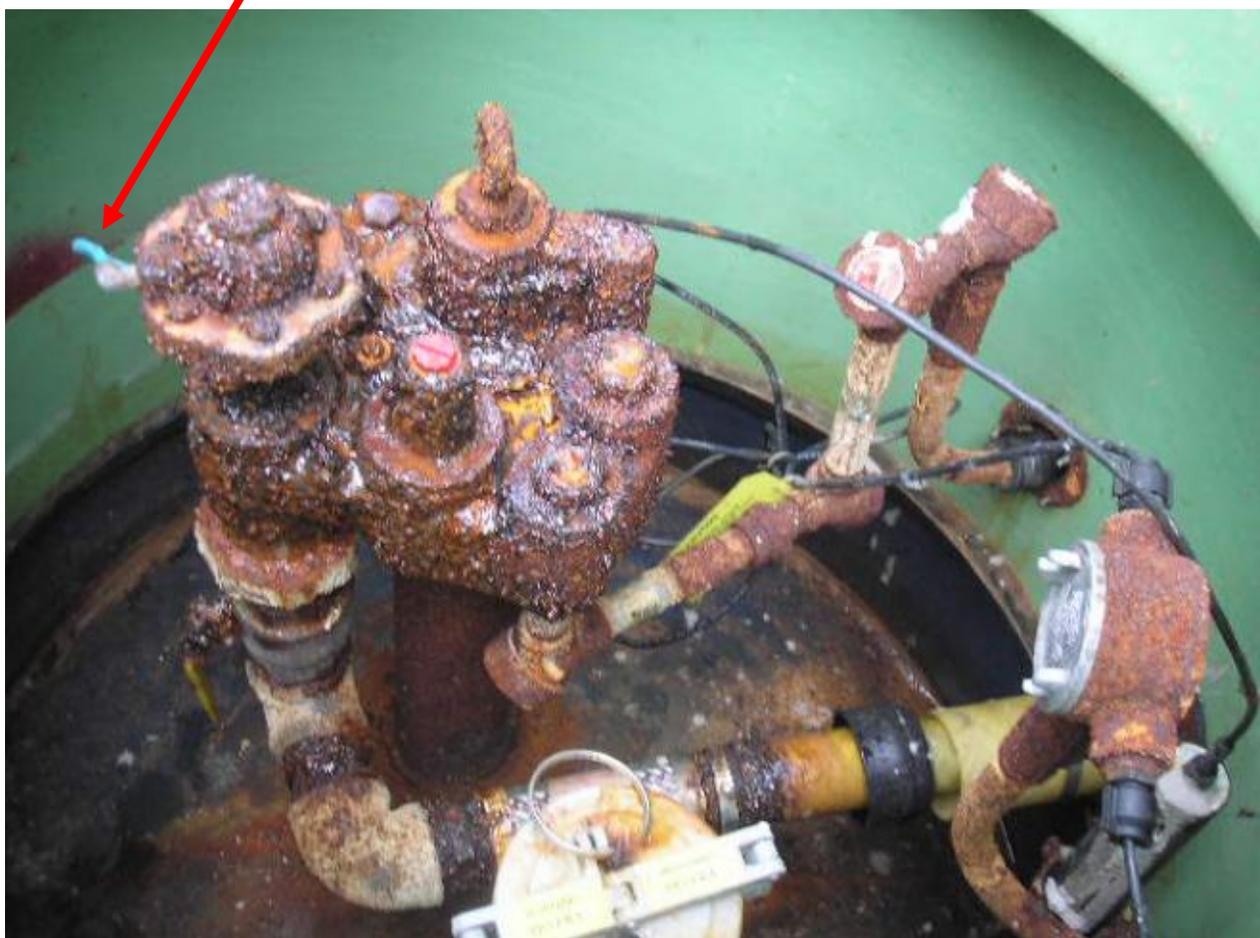
3/29/2011



Sump 26

Regular Gasoline

3/29/2011



Sump 33

Regular Gasoline

07/27/2011



Sump 36

Premium Gasoline

Date NA



Sump 37

Regular Gasoline

02/02/ 2011



Sump 38

Premium Gasoline

9/9/2011



Sump 39

Premium Gasoline

9/11/2011



Sump 40

Premium Gasoline

9/9/2011



Sump 41

Regular Gasoline

9/9/2011

Note gap where corrosion has flaked off.



Sump 42

Regular Gasoline

9/9/2011



Sump 43

Premium Gasoline

9/9/2011



Sump 44

Regular Gasoline

9/9/2011



Sump 45

Premium Gasoline

9/9/2011



Sump 46

Premium Gasoline

9/9/2011



Sump 47

Regular Gasoline

9/9/2011



Sump 48

E85 Gasoline

9/9/2011



Sump 49

Regular Gasoline

9/9/2011



Sump 50

Regular Gasoline

9/9/2011



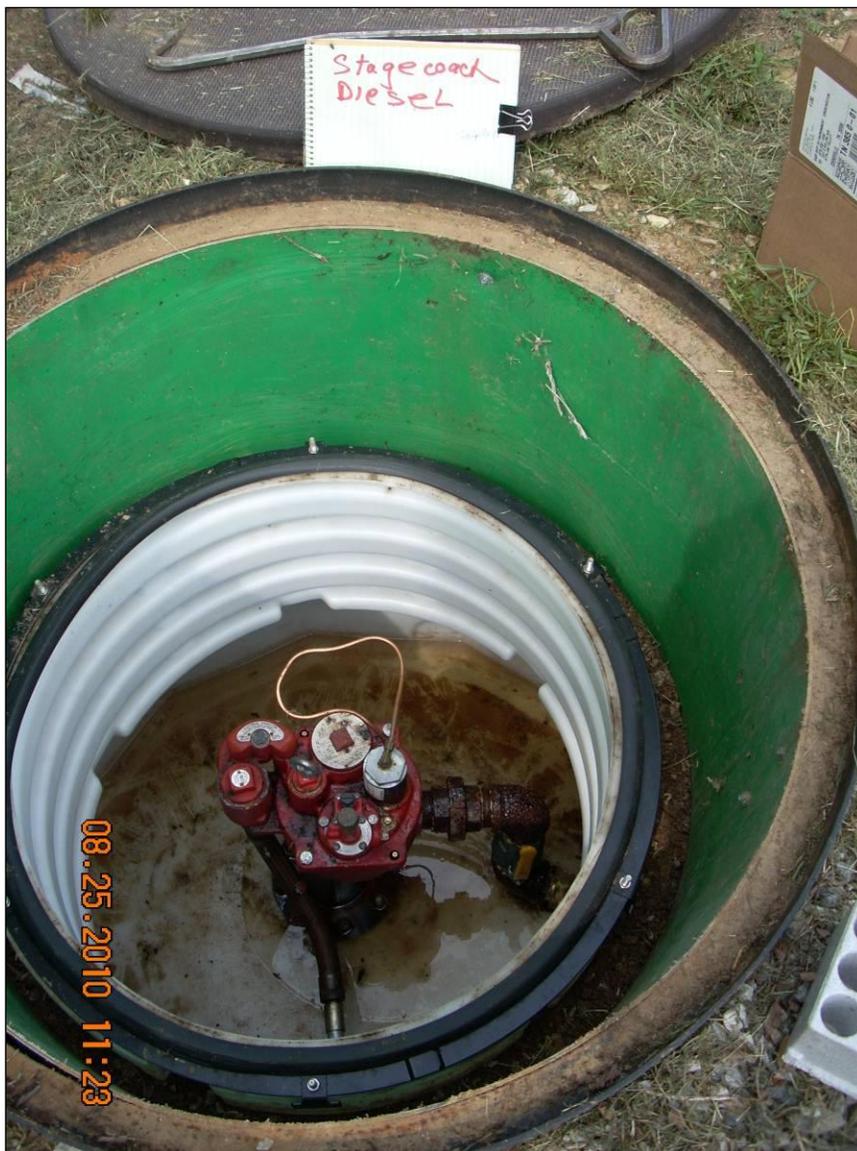
Part 3. Sumps that were not scored.

Sump 6

Diesel Fuel

Not scored because no vapor samples were taken.

8/25/2010



Sump 16

2/4/2011

Regular Gasoline



Sump 18

2/4/2011

Premium Gasoline



Sump 27

Regular Gasoline

7/18/2011



Sump 28

Mid Grade Gasoline.

Not scored because there was not vapor samples.

7/27/2011



Sump 29

Premium Gasoline

7/27/2011



Sump 34

Premium Gasoline

7/27/2011



Sump 35

Premium Gasoline

7/27/2011



Part 4. Calibration of Passive Diffusion Samplers

Description of the Passive Diffusion Samplers

The samplers were designed to provide an integrated determination of the average concentrations of ethanol and acetic acid in air in the sump when the sumps were sealed up and the concentrations in air were in their ordinary condition. The construction of the samplers is depicted in Figure 1. They were constructed using ordinary 40 mL volatile organic analysis (VOA) vials. The vials contained 1% trisodium phosphate dodecahydrate (TSP) as a preservative to prevent biodegradation of the ethanol or acetate in the sampler. The TSP maintained a pH of 10.5, which will prevent the growth of bacteria that degrade ethanol or acetate. The vials were filled with distilled water containing TSP in the laboratory. They were shipped to the field sites with a Teflon-faced silicone rubber septum. This is the septum that is used in VOA samples to contain organic compounds in water samples. At the field site, the sampling technician replaced the conventional screw cap containing a Teflon-faced silicone rubber septum with a screw cap containing a diffusion membrane. The membrane was composed of Supor (polyethersulfone). It contained perforations with a maximum diameter of 0.2 μm . The samplers were left in place for approximately one month. When they were recovered, the diffusion membrane was replaced with a screw cap containing a Teflon-faced silicone rubber septum, and the samples were shipped back to the R.S. Kerr Center in Ada, OK for analysis.

The samples were analyzed for ethanol using EPA Method 8260B. Acetate was analyzed using High Performance Liquid Chromatography.

Calibration of the Passive Diffusion Samplers

The rate of accumulation of ethanol or acetate in the water in the samplers was controlled by diffusion across the membrane. As long as the concentration inside the sampler is low compared to the concentration outside the sampler, the concentration gradient across the membrane is constant during sampling. As a result, the rate of accumulation should be proportional to the concentration of ethanol or acetate in the vapors outside the sampler. If the rate of accumulation is constant at a given concentration of ethanol or acetate in the air being sampled, the total accumulation of ethanol or acetate in the sampler is a linear function of the time of incubation.

The passive diffusion samplers were calibrated by exposing them to air above water containing known concentrations of ethanol or acetate. Duplicate samplers were incubated in sealed 2 L jars containing 1 L of calibration water. The samplers were supported in a manner that exposed the membrane to the headspace above the calibration water.

There were four treatments. The calibration water in the first treatment was commercial vinegar with a nominal concentration of 60,000 mg/L acetate. The second treatment was a dilution of commercial vinegar containing 1,000 mg/L acetate, and adequate HCl to bring the pH below 2. The third treatment was ethanol in water containing 6,000 mg/L. The third treatment was preserved with 1% TSP. The

fourth treatment was 1,000 mg/L ethanol in water. The fourth treatment was also preserved with 1% TSP. One jar from each treatment was sampled after 0, 7, 14, 21, and 28 days of incubation.

Figure 2 presents the measured concentrations of ethanol in the calibration water at each sampling period. Figure 3 presents the measured concentrations of acetate in the calibration water at each sampling period. The quality of the data was controlled in part by continuing calibration checks. Data were reported for ethanol if the continuing calibration check standards were within $\pm 20\%$ of the nominal value. Data were reported for acetate if the continuing calibration check standards were within $\pm 15\%$ of the nominal value. There was no evidence of loss or degradation of ethanol or acetate in the calibration waters. The agreement between duplicate diffusion samplers in each sampling period was acceptable considering the allowed variability in the individual analyses.

Figure 4 presents the accumulated concentration of ethanol or acetate in the passive diffusion samplers as a fraction of the measured concentration in the calibration water. There was a sixty fold difference in the concentrations of acetic acid in treatments 1 and 2. Over this range, the fractional recovery of acetate was in general agreement. There was a six fold difference in the concentrations of ethanol in treatments 3 and 4. After 28 days of incubation, the average recovery in treatment 4 was 28% less than the average recovery in treatment 3. The difference is statistically significant with a probability of error of 2.5%; however the bias has no practical affect on the data evaluation. Table 1 of *Corrosion in a STP Sump: What Causes It and What Can You Do About It?* indicates that the geometric means of samples with corrosion vary from the means of samples without corrosion by a factor near 100 fold. A factor near 1.28 fold will have no important affect on the comparison in Table 1.

Some of the passive diffusion samplers were returned to the laboratory with a significant air headspace. Presumably, water evaporated from the samplers during incubation in the sump. The water loss was never more than 50% of the total volume of the sampler. To determine if water loss affected the performance of the sampler, the calibration was repeated for acetate at 1000 mg/L in the source water using passive diffusion samplers that were half filled with water and samplers that were entirely filled with water. Results are presented in Figure 5. There was no difference in the performance of samplers filled with water and samplers half filled with water. The loss of water had no detectable effect on the accumulation of acetate in the samplers.

Concentrations in Water and Air

The biodegradation of ethanol to acetic acid and the chemical reaction between acetic acid and metallic copper occur in an aqueous environment. For this reason, the concentrations in air are expressed as an equivalent concentration in water, based on the equilibrium distribution of ethanol or acetic acid between air and water. The concentration in air in more conventional units can be recovered using Figure 6 and Figure 7. Figure 6 compares the concentrations of ethanol that would be expected in air based on equilibrium with concentrations in water assuming a Henry's Law constant for ethanol and water of 190 moles per liter in water per atmosphere. Figure 7 compares the concentrations of acetic acid that would be expected in air based on equilibrium with concentrations in water assuming a Henry's Law constant for acetic acid and water of 5500 moles per liter in water per atmosphere.

Validation of the Passive Diffusion Sampler

To independently validate the predictions of the passive diffusion sampler, measured concentrations of acetate or ethanol in the sump water were compared to predicted concentrations based on the acetate or ethanol that accumulated in the samplers. The comparison assumed that the concentrations of acetate and ethanol in the sump water and in the air above the sump were stable over the thirty days of incubation.

The results for acetate are presented in Figure 8. At concentrations below 10 mg/L there was more scatter and these data are not shown. Most of the corrosion occurred in sumps with more than 10 mg/l of ethanol or acetate (Figure in 3 of *Corrosion in a STP Sump 1: What Causes It and What Can Be Done About It?*). In Figure 8 the correspondence between the concentrations of acetate measured in water and concentrations predicted from the vapors samplers was good.

The results for ethanol are presented in Figure 9. As was the case for acetic acid, at concentrations below 10 mg/L there was more scatter and these data are not shown. The association between the concentrations of ethanol measured in water and predicted from the vapors samplers was not as good as was the case for acetic acid. There tended to be more ethanol in the water in the sampler. This may reflect degradation of ethanol to acetate in the sump water. The water in the sampler was preserved with trisodium phosphate and the ethanol did not degrade in the samplers. In any case the association was close enough to indicate that the passive samplers could make a useful prediction of the concentration of ethanol in condensation water in the sumps. The concentration in the sump was within an order of magnitude of the predicted concentration in the condensation water.

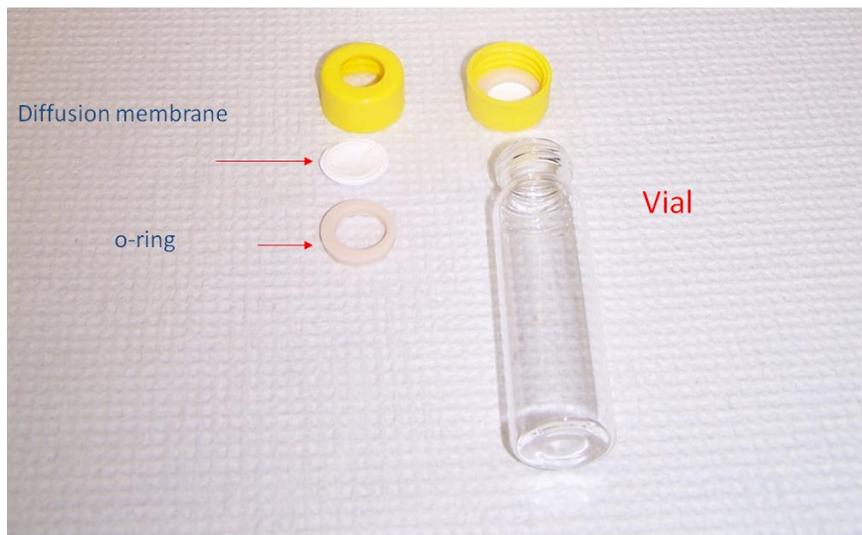


Figure 1. The components of the passive diffusion samplers.

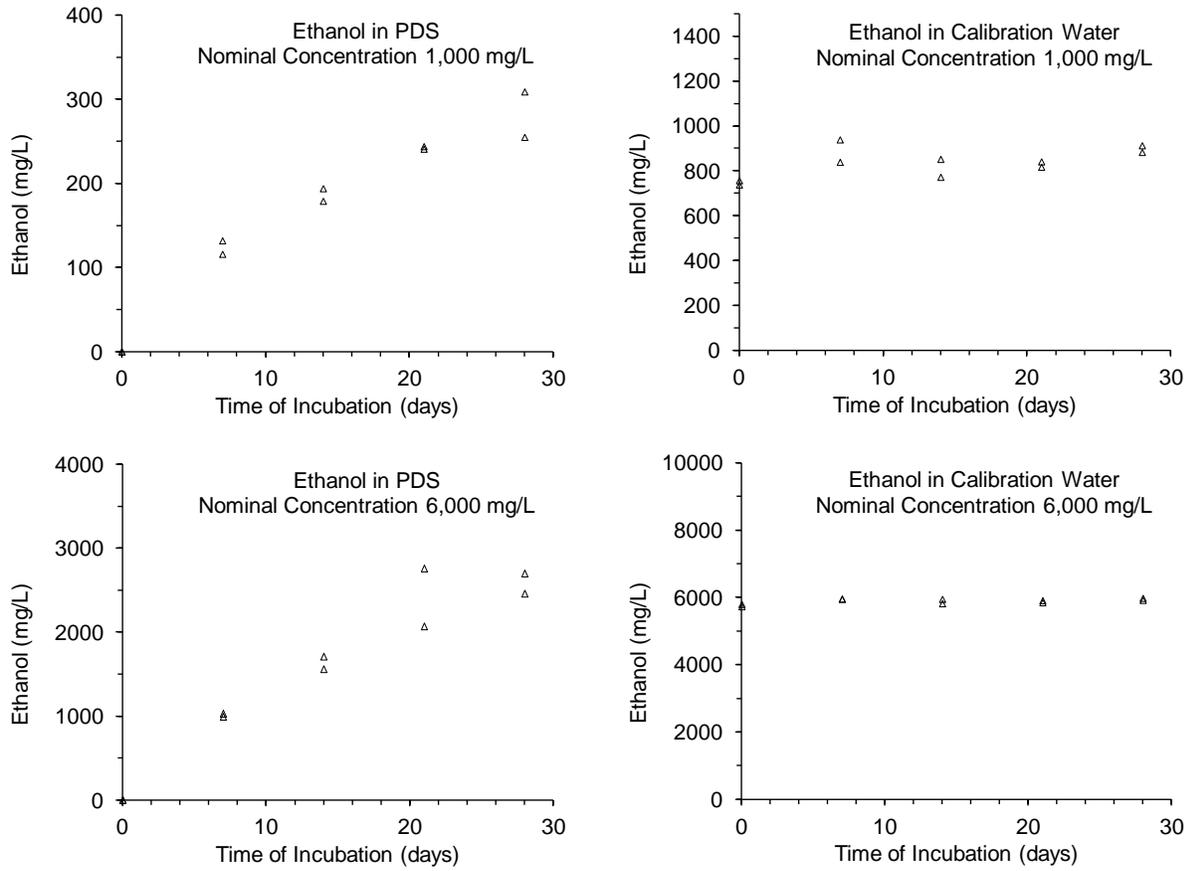


Figure 2. Concentrations of ethanol in the calibration water and in the passive diffusion samplers.

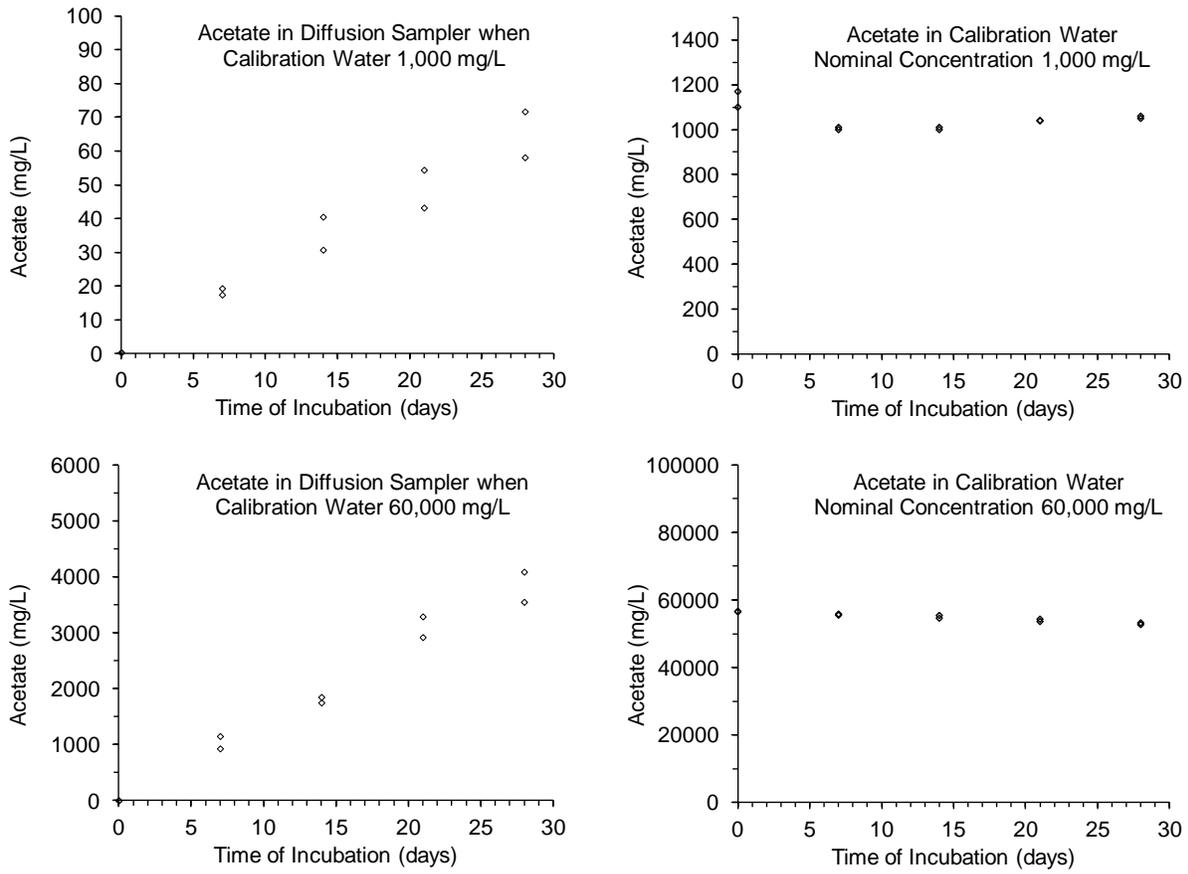


Figure 3. Concentrations of acetate in the calibration water and in the passive diffusion samplers.

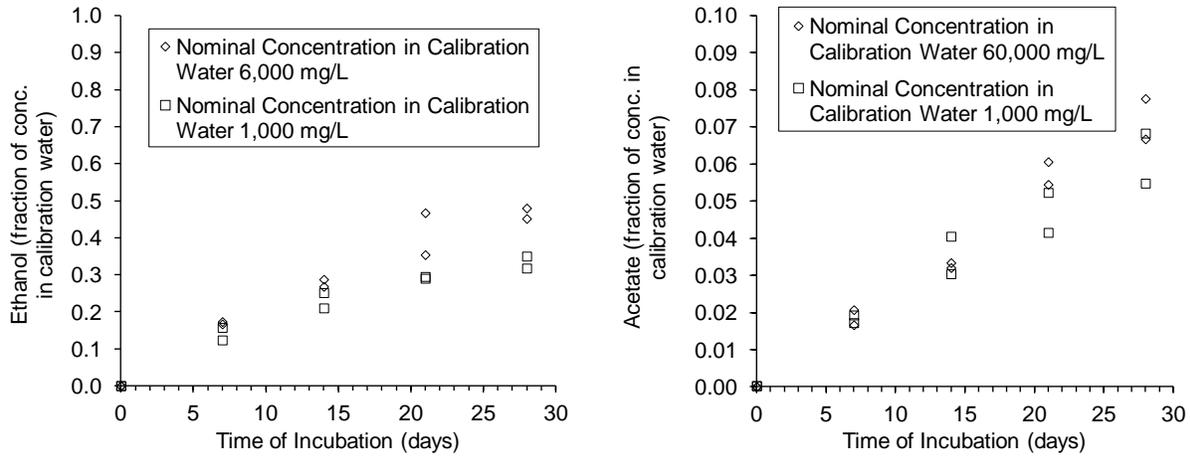


Figure 4. The fraction of the concentration of ethanol or acetate in the calibration water that was accumulated in the passive diffusion sampler over 28 days of incubation.

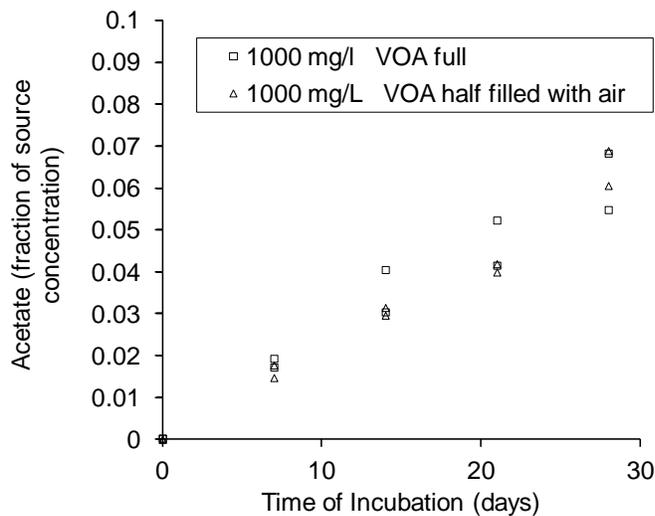


Figure 5. The fraction of the concentration of acetate in the calibration water that was accumulated in the passive diffusion sampler over 28 days of incubation if the passive diffusion sampler was half filled with air.

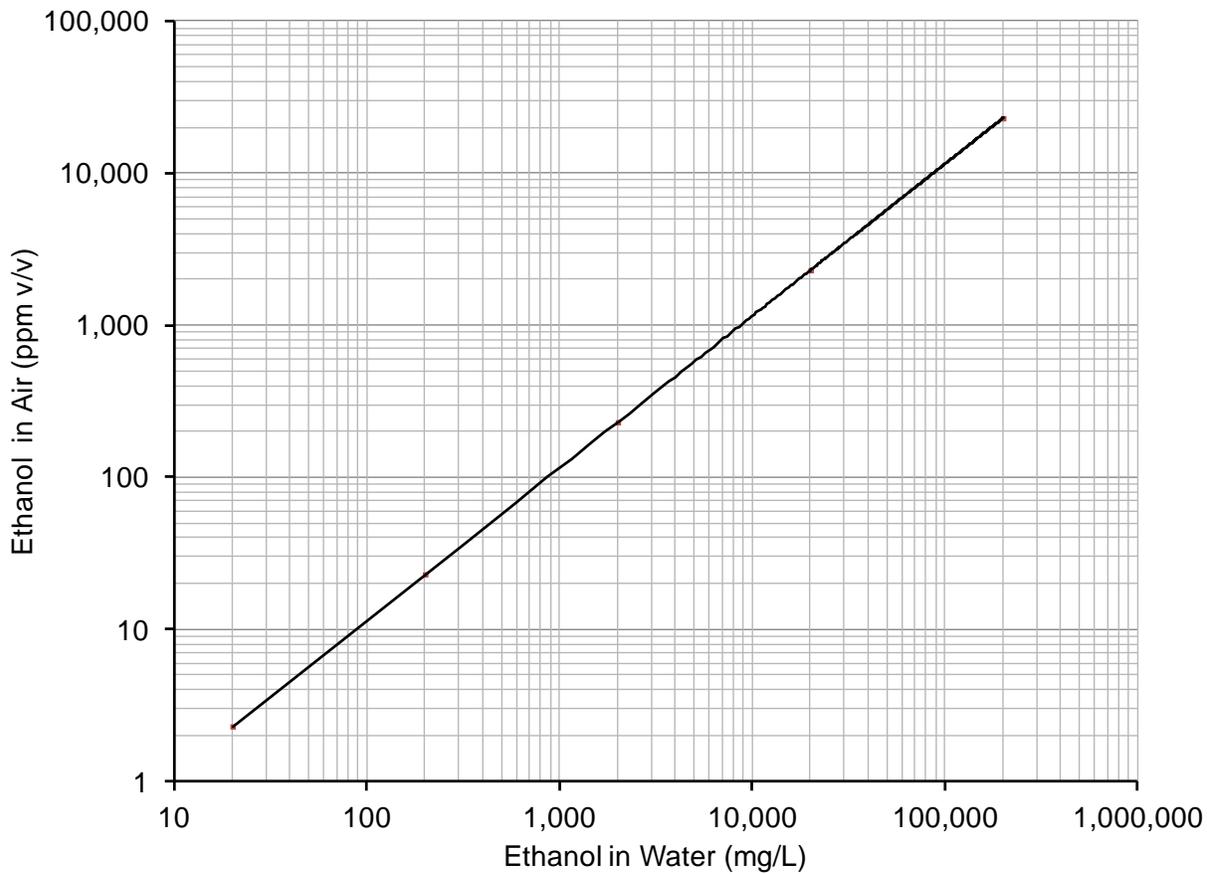


Figure 6. Concentrations of ethanol in air in equilibrium with concentrations in water.

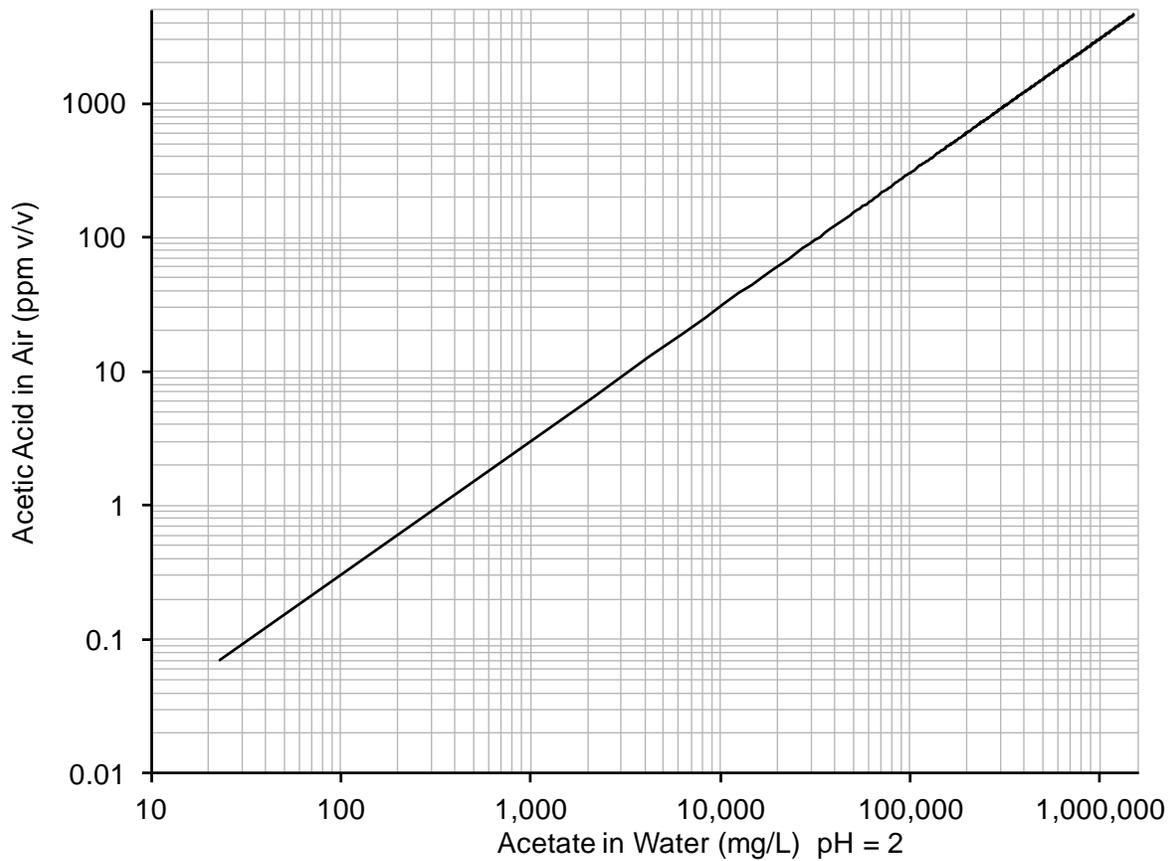


Figure 7. Concentrations of acetic acid in air in equilibrium with concentrations of acetate in water.

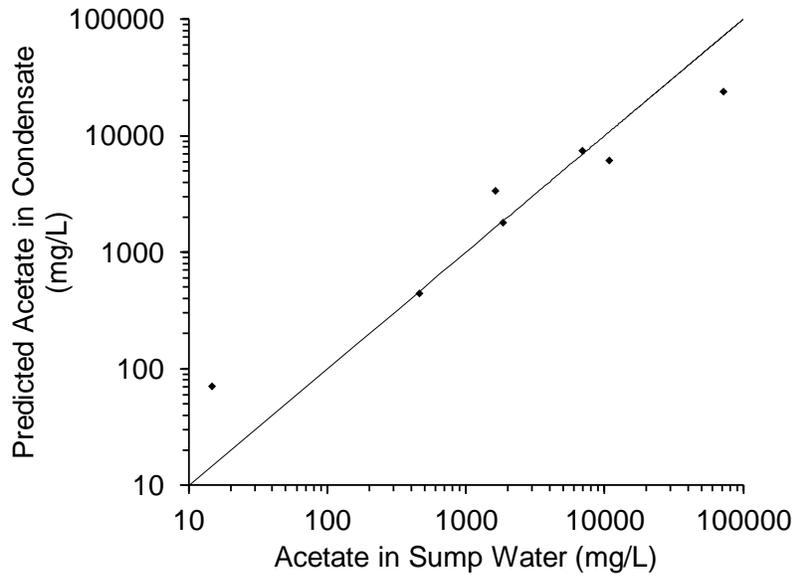


Figure 8. Comparison of measured concentrations of acetic acid in sump water to predicted concentrations in condensate water based on the measured concentrations in the vapor sampler.

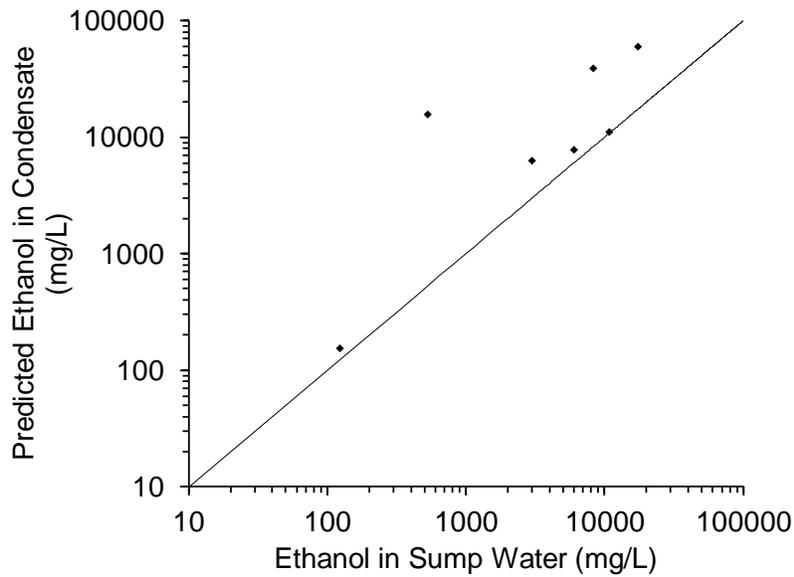


Figure 9. Comparison of measured concentrations of ethanol in sump water to predicted concentrations in condensate water based on the measured concentrations in the vapor sampler.